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ORIGINAL RESEARCH ARTICLE

Enhancement of Titanium Nitride-Specific Capacitance Using Rapid Thermal Sulfurization

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The present study examines the effects of thermal sulfurization on enhancing the electrochemical storage capabilities of titanium nitride (TiN) as a potential electrode material for electrochemical capacitors. The thermal sulfurization process was carried out at various temperatures (350, 500, and 650 °C). The XPS analysis approved the effects of this process in the incorporation of sulfur into the surface and subsurface regions of the electrodes. Importantly, compared to untreated pristine TiN film, the sulfurized TiN electrode exhibited a notable improvement in areal capacitance. Specifically, the sulfurized TiN electrode achieved an impressive areal capacitance of up to 15 mF cm^{-2} when tested at a scan rate of 5 mV s^{-1} (equivalent to a volumetric capacitance of 350 F cm^{-3}) in a 1 M KOH electrolyte solution. Furthermore, it demonstrated high cycle stability, retaining 96% of its capacitance over 10,000 consecutive cycles. The study also delved into the surface chemistry and morphology of the electrodes before and after sulfurization, establishing a correlation with the electrochemical properties of these electrodes. These findings suggest that sulfur doping in transition metal nitrides holds promise as a viable strategy for developing high-performance materials for electrochemical energy storage applications.

Keywords electrochemical capacitors, surface chemistry, thermal sulfurization, titanium nitride

1. Introduction

Supercapacitors represent a new generation of electrochemical components for energy storage. These relatively new components occupy a truly intermediate position between electrolytic capacitors and electrochemical accumulators in terms of specific energy and power. Their advantage lies in the significant energy they can store directly; unlike capacitors, they are able to store directly in their electrical form, thus preserving the immediate availability of energy. Electrochemical capacitors (ECs), often referred to as supercapacitors or ultracapacitors, stand out as highly promising energy storage systems that effectively convert electrochemical energy into electricity (Ref 1-4). Unlike conventional lithium-ion batteries, ECs excel in delivering energy rapidly, showcasing their superior power density. Additionally, they demonstrate remarkable longevity, outlasting the typical operational lifetimes of lithium-ion batteries (Ref 1-6). However, despite these advantages, ECs still exhibit a moderate energy density, making them less competitive when compared to Li-ion batteries (Ref 3-6). Consequently, the current focus within the EC research community is directed toward elevating their energy density without compromising power density or cycling life.

It is possible to determine the energy density (E) of ECs using the following formula $E = 1/2\ CV^2$, where C denotes specific capacitance, and V signifies the potential window (Ref 1-3). Consequently, there are two primary avenues for enhancing energy density: either by expanding the operational potential window, achieved through electrolyte selection, or by improving the specific capacitance (Ref 1-5). Given that the electrochemical processes in ECs predominantly occur at and subsurface of the electrode (Ref 1, 7, 8), enhancing specific capacitance can be achieved through two strategies: (i) augmenting the surface area or (ii) engineering the surface chemistry (Ref 1, 4, 5, 7-9). While many researchers concentrate on augmenting surface area through nanostructuring, relatively few efforts are dedicated to the intricate task of tailoring the surface chemistry of materials to enhance specific capacitance and, consequently, energy density (Ref 7-9). Until now, most surface modification endeavors have focused on carbon-based materials like carbon nanotubes (Ref 10), graphene (Ref 11), and a handful of metal oxides, such as manganese oxide (Ref 12).

The surface modification process typically involves the introduction of one, two, or even three heteroatoms, including, nitrogen (Ref 11), oxygen (Ref 13), hydrogen (Ref 14), or sulfur (Ref 15). These heteroatoms play a pivotal role in enhancing electrochemical energy storage by providing new active sites for OH adsorption in most cases (Ref 14, 15).

Recent investigations have turned to transition metal nitrides (TMNs), such as MoN (Ref 16), CrN (Ref 17) VN (Ref 18), and TiN (Ref 19, 20), as potential pseudo-capacitive materials owing to their superior electrical conductivity compared to their

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